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Facile synthesis of gold-capped TiO_2 nanocomposites for surface-enhanced Raman scattering

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HIGHLIGHTS

- Au–TiO_2 nanocomposites with different morphologies were fabricated.
- Au–TiO_2 nanopore shows pronounced SERS compared with nanotube and nanolace.
- The size of the gold nanocaps on Au–TiO_2 nanopore was tailored to optimize the SERS.
- FDTD simulations indicate excellent SERS attributes to the high density of hot spots.
- Au–TiO_2 nanocomposites prove to be recyclable substrates for SERS detection.

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ABSTRACT

A convenient technique was developed to fabricate gold-capped TiO_2 nanocomposites as robust, cost-efficient and recyclable surface-enhanced Raman scattering (SERS) substrates. The morphologies of obtained nanocomposites exhibit nanotube, nanolace, and nanopore nanostructures by adjusting TiO_2 anodization parameters. As an illustration, dramatic enhancement is achieved using Rhodamine 6G as a molecular probe. Owing to activation by the incident laser beam, the localized electromagnetic field on the nanocomposite surface can be enhanced subsequently amplifying the Raman signal. The topography can be further tuned to optimize the enhancement factor by adjusting the time of gold evaporation. Finite-difference time-domain calculations indicate the nanopore structure may possess excellent SERS characteristic due to the high density of hot spots. In addition, the substrate can be self-cleaned under ultraviolet irradiation due to the superior photocatalytic capacity of the Au–TiO_2 nanocomposites. Our Au–TiO_2 nanocomposites with highly SERS-active properties and recyclability shows promising applications in the detection and treatment of pollutants.

1. Introduction

Nanocomposites based on noble metal nanoparticles are attracting ever-increasing interest in nano- and bio-technology due to the synergic combination of their versatile surface chemistry and properties. In a number of reports [1–3], the deposition of small amounts of noble metal on the semiconductor surface has been proposed as an effective method to increase the quantum yield. In particular, Au–TiO_2 system has been proven to perform a significant enhancement when used in photoelectrochemistry [4,5], photocatalysis [6,7] and surface-enhanced spectroscopy [8–10]. Furthermore, since gold claims an excellent application in the field of surface-enhanced Raman scattering (SERS) and TiO_2 shows various possible morphologies, more Au–TiO_2 nanocomposites for SERS were fabricated, such as Raman reporter-embedded TiO_2 core-Au shell nanoparticles [11] and Au-mesopourous TiO_2 molecular sieves [12]. On the other hand, TiO_2 has been extensively used in photocatalytic degradation of organic pollutants, thus it is more desirable to optimize characteristics of Au–TiO_2 nanocomposites for recyclable SERS substrates, aiming at environmental problems related to the detection and treatment of pollutants [13].

Herein, we present a simple nanotechnique to fabricate gold-capped TiO_2 nanocomposites as robust, cost-efficient and recyclable SERS substrates. This technique has three distinct advantages. TiO_2 porous nanostructures with three different surface morphologies (nanotube/nanolace/nanopore) were prepared by adjusting TiO_2 anodization parameters, the substrate performance

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can be optimized by tailoring the plasmonic geometries and the Au–TiO_2 nanocomposites prove to be recyclable for SERS detection.

2. Experimental

High-purity Ti foils with 1-mm thickness were cleaned by acetone to degrease the surfaces, followed by chemical polishing for 5 min in a mixture of hydrofluoric acid (40%), nitric acid (65%), and water with volume ratio of 1:4:5, to further remove surface impurities. After rinsing in distilled water and drying, the Ti foils were anodized in a fresh electrolyte under a constant DC voltage of 60 V at 25 °C. The electrolyte consists of a mixture of ethylene glycol and deionized water (100:2) containing 0.3 wt% NH_4F. In order to obtain more regular nanostructure arrays with different morphologies, two-step anodizing processes were adopted. Firstly The Ti foils were anodized for 3 h, followed by polarizing with a cathodic pulse in 1 M H_2SO_4 at −3 V to remove the TiO_2 nanolayer [14]. Then immediately, the Ti samples were anodized at different anodization potentials and times (60 V, 3 h; 30 V, 1 min, 60 V, 1 h; 60 V, 1 h) to fabricate TiO_2 nanotubes, TiO_2 nanolaces and TiO_2 nanopores, respectively. Gold nanocap films were prepared on the TiO_2 nanostructures by a vacuum thermal evaporation system (Technol ZHD-400). It should be noted that all the deposition process is performed at a hyperslow rate of 0.01 nm/s, reducing the impact on TiO_2 nanostructures. The film thickness was controlled by film-thickness monitor (Taiyao FTM-V).

Scanning electron microscopy (SEM, FEI Inspect F50) was used to investigate the morphology of TiO_2 nanostructures. Commercial finite-difference time-domain (FDTD) software (CST MWS 2010) was used to calculate the electromagnetic (EM) field properties of nanostructures. The Drude model was employed to describe the properties of materials. The parameters of the nanocomposites in the simulation were set to the parameters in our experiments. The wavelength of the incident wave was set to 514 nm. The Raman measurements were performed on a Jobin Yvon LabRAM HR800 micro-Raman spectrometer with the 514-nm laser line at room temperature. The diameter of probe is ~1 mm with a 50× objective lens and the incident power at the samples of 3 mW. A 10^{-5} M

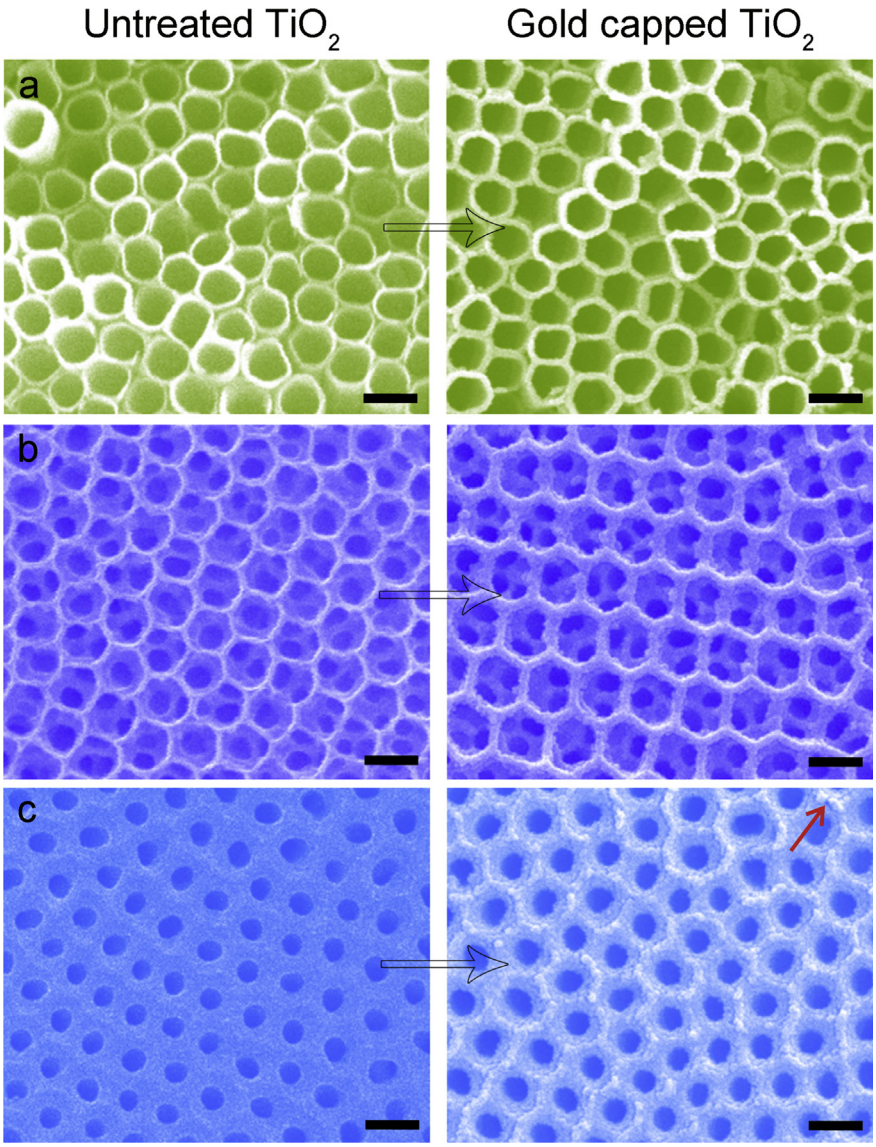

Fig. 1. SEM images of the TiO_2 nanostructures (a: nanotube/b: nanolace/c: nanopore) before and after gold evaporation (thickness: 20 nm). The scale bar is 200 nm. The red arrow in Fig. 1(c) shows one of the protrusions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)